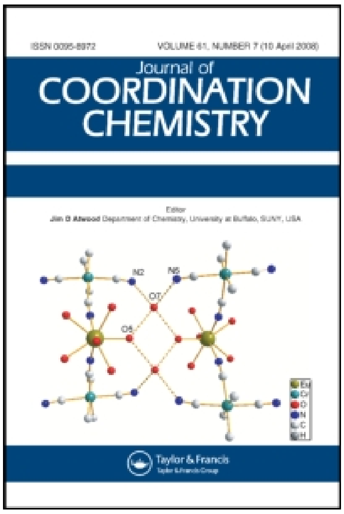

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SOME PALLADIUM(II) COMPLEXES OF 1,2-BIS(MERCAPTO)ORTHOCARBORANE

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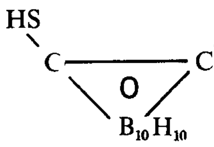
Coordination compounds of the type Pd(DMC)L and [Pd(DMC)$_2$]C where DMC is 1,2-bis(mercapto)-*o*-carborane, L = 1-diphenylphosphino-*o*-carborane (HPC), 1,2-bis(diphenylphosphino-*o*-carborane (NPC) and C = H$^+$ or tetraethylammonium cation, have been prepared and characterized by IR, Raman and electronic spectroscopy, magnetic and conductivity measurements. DMC behaves as a bidentate sulphur donor ligand and the tertiary phosphine (HPC) and ditertiary phosphines (DPC and NPC) are bonded through the phosphorous atoms to produce a planar PdS$_2$P$_2$ skeleton of C_{2v} symmetry.

Keywords: palladium, phosphines, dithiol, complexes, synthesis

INTRODUCTION

In previous papers,[1–3], we reported the preparation characterization and spectroscopic data of a number of complexes of Pd(II), Co(II) and Ni(II) with tertiary and ditertiary phosphines containing *o*-carborane ($B_{10}H_{10}C_2$) group as a backbone. The vibrational and electronic spectra showed that the palladium(II) and nickel(II) complexes possess square-planar geometry whereas those of cobalt(II) have a pseudotetrahedral one.

The tertiary phosphine 1-diphenylphosphino-*o*-carborane (HPC) produced trans-planar complexes of the type Pd(HPC)$_2$X$_2$ where X = Cl or Br, whereas the ditertiary phosphines 1, 2-bis(diphenylphosphino)-*o*-carborane (DPC) and 1-bis(dimethylammino)phosphino-2-diphenylphosphino-*o*-carborane (NPC) produce the expected cis-planar complexes of the type Pd(DPC or NPC)X$_2$. In the present work, we report a new series of complexes of a ligand derived from the *ortho*-carborane, *i.e.*, 1,2-bis(mercapto)-*o*-carborane (DMC).



DMC

Mixed complexes containing the phosphines PPh$_3$, HPC, DPC and NPC and the DMC ligand have been prepared and spectroscopically characterized.

EXPERIMENTAL

Preparative

1,2-bis(mercapto)-*ortho*-carborane (DMC) was prepared as follows. To a cooled ether solution containing 0.05 mol of *o*-carborane ($B_{10}H_{12}C_2$) and 0.1 mol of *n*-buthyllithium, 0.11 mol of elemental sulphur was added. The yellow solution was stirred for one hour and 0.15 mol of HCl in 30 cm^3 of water added. After stirring for 15 minutes at room temperature with 200 cm^3 of ether, the ether extract was dried with $MgSO_4$ and then evaporated to dryness. The compound was recrystallized from petroleum-ether (30/60) with a 90% yield. Melting point: 265-267°.

The coordination compounds of DMC with Palladium(II) and the mixed DMC-phosphine complexes were prepared by a general method. To a suspension of 0.52 mol of $Pd(C_6H_5CN)CL_2$ in 50 cm^3 of benzene, the stoichiometric amount of DMC (1.05 mmol) was added. The mixture was stirred for 30 minutes and the red solid filtered off, washed and dried. In the preparation of the mixed ligand complexes, 0.52 mmol of DMC and the stoichiometric amount of the corresponding phosphine were added. In each case a red solid was obtained with yields better than 70%. The $Pd(DMC)(PPh_2)_2$ complex is yellow.

Physical Measurements

The IR, Raman and electronic spectra and magnetic and conductivity measurements were carried out as described previously.[3] Table I shows the analytical conductivity and magnetic data for the complexes reported.

RESULTS AND DISCUSSION

The conductivity data show that the complexes I and II are 2:1 electrolytes in dimethylformamide (DMF) according with the range 130-170 mhos cm^2 mol^{-1} given in the literature.[4] The compounds III to VI are typical non-electrolytes in this solvent (accepted range 0-65 mhos cm^2 mol^{-1}). The magnetic measurements show that the compounds are diamagnetic in agreement with a planar geometry for these d^8 species.

The mid-IR spectra show the typical absorptions of the ligands HPC, DPC, NPC and DMC. In general the absorption of the *o*-carborane cage shows very small shifts implying that the cage is not perturbed on coordination. The C-S stretching modes in

TABLE I

Analytical, conductivity and magnetic data for the DMC complexes of palladium(II)

Compound[a]	No	C %	H %	N %	S %	Pd %	$\Lambda_M 20°$	corr $\chi_M \times 10^6$
$H_2[Pd(DMC)_2]$	I	8.8 (9.2)[b]	4.6(4.3)			19.1(20.5)	134	40
$[(C_2H_5N)_2][Pd(DMC)_2]$	II	30.6(30.8)	7.4(7.8)	3.0(3.6)		13.7(13.7)	131	63
$[Pd(DMC)(PPh_3)_2]$	III	54.0(54.5)	4.0(4.8)		7.8(7.8)	12.8(12.7)	72	61
$[Pd(DMC)(HPC)_2]$	IV	38.0(37.1)	5.0(5.4)		7.0(6.6)	11.4(11.0)	49	42
$[Pd(DMC)(DPC)]$	V	36.5(36.8)	4.6(4.9)		7.3(7.4)	11.3(12.9)	44	30
$[Pd(DMC)(NPC)]$	VI	31.4(31.6)	5.4(5.6)	3.7(3.7)	8.1(8.4)	13.7(14.0)	37	71

[a] DMC = $B_{10}H_{10}C_2S_2$; PPh$_3$ = $C_{18}H_{15}P$; HPC = $B_{10}H_{21}C_{14}P$; DPC = $B_{10}H_{30}C_{26}P_2$; NPC = $B_{10}H_{32}C_{18}P_2N_2$..

[b] Calculated values given in parentheses.

TABLE II
Selected IR bands for the DMC complexes of palladium(II)

Compound	γ(P-C(Phenyl))	γ(C-N)	γ(P-N)	Planar def. of C_6H_5 group
III	1094s			1431s
IV	1096f			1437s
V	1099w			1445s
VI	1096m	1274w	985m	1435m
		1190w	971m	

TABLE III
Pd-P and P-S stretching mode frequencies in the DMC complexes of palladium(II).

Compound[a]	γ(Pd-P)		γ(Pd-S)	
	IR[a]	RAMAN	IR	RAMAN
I				368s
			332m	340w
II				365s
			334w	346w
III	443m	443w	361m	367s
	426m	431w	324s	318w
IV	438m	453w	367w	366s
	410w	418w	320w	344w
V	440m	463w	340s	364s
		426w		331w
VI	446m	463m	366w	363w
	418w	424w	322w	332w

[a] Ir spectra recorded in CsI pellets.

the DMC ligand are covered by other stronger absorptions of the cage.[5] Sandhy *et al.*,[6] assigned a strong absorption at *ca* 1090 cm^{-1} to the P-C (phenyl) stretching mode in the ligand bis(diphenylphosphino)ethane (DPPE). This mode shifts by *ca* 10 cm^{-1} upon coordination and hence it has been used as a criterion for phosphorous coordination in the DPPE complexes. The HPC, DPC and NPC complexes show this mode to be shifted by *ca* 6–9 cm^{-1} implying that the ligands are coordinated through the phosphorous atoms. Table II shows some selected IR bands of the complexes reported. Complexes III to VI show the planar deformation mode of the phenyl groups in the 1445–1430 cm^{-1} region. This mode is also shifted by *ca* 7 cm^{-1} upon coordination.

The far-IR and Raman Spectra show the Pd-P and Pd-S stretching modes along with bands due to ligand and lattice modes. The γ(Pd-P) and γ(Pd-S) modes have been assigned by comparison with other closely related molecules.[1,2,3,7,8] Table III shows these modes and their tentative assignments. If we assume a C_{2v} symmetry for the PdP_2S_2 skeleton in the mixed complexes of DMC, the seven in-plane modes are distributed as follows: $4A_l + 3B_l$. Both, the symmetric (A_l) and antisymmetric (B_l) Pd-P stretching modes are IR and Raman active and are observed at *ca* 400 cm^{-1}, whereas the corresponding Pd-S ($A_l + B_l$) show up at *ca* 350 cm^{-1}. The high frequency bands in the

TABLE IV
Electronic spectral data for the DMC complexes of palladium(II)[a].

Complex	λmax (nm)[b]	Assignment[c]
I	340(4582)	$M \rightarrow L^*$
	317(5726)	$L \rightarrow M$
II	337(5528)	$M \rightarrow L^*$
	307(5563)	$L \rightarrow M$
III	311(10028)	$M \rightarrow L^*$
	276(8616)	$\pi \rightarrow \pi^*$ (phenyl group)
IV	335(12060)	$M \rightarrow L^*$
	316(14025)	$L \rightarrow M$
V	327(5393)	$M \rightarrow L^*$
	306(5818)	$L \rightarrow M$
VI	327(6200)	$M \rightarrow L^*$
	308(6815)	$L \rightarrow M$

[a]Spectra in DMF. [b]Extinction coefficients given in parentheses; M^{-1} cm^{-} [c]$M \rightarrow L^* = xy(\pi^*) \rightarrow L(\pi^*)$ and/or xz, $yz(\pi^*) \rightarrow L(\pi^*)$; $L \rightarrow M = L(\pi) \rightarrow x^2\text{-}y^2(\sigma^*)$ and/or $L(\sigma) \rightarrow x^2\text{-}y^2(\sigma^*)$.

IR and Raman have been assigned to the symmetric γ(Pd-P) and γ(Pd-S) stretches by analogy with related complexes.[9] The observation of two γ(Pd-P) and two γ(Pd-S) modes confirm the assumption of a planar C_{2v} symmetry for these species.

The anionic complexes I and II possess D_{4h} symmetry and accordingly the (Pd-S) $(A_{1g} + B_{2g} + E_u)$ are to be observed in the Raman $(A_{1g} + B_{2g})$ and the IR (E_u). As predicted by the selection rules, only one band is observed in the IR and two bands in the Raman confirming square-planar geometry for the PdS_4 skeleton.

The electronic spectra of these DMC complexes of palladium(II) show a couple of bands which have been assigned by comparison with some dithioacetylacetonates[10] maleonitrile dithiolate[11] and 2,3 dimercaptopropanol[12] complexes.

The electronic spectra show two bands located at *ca* 340 and 310 nm; according to Gray *et al*,[13] these bands can be assigned to M → L or L → M charge transfer transitions. The three d-d transition that should accompany a planar complex are generally covered by the strong CT bands. Thus, the lowest energy band could be due to a $M \rightarrow L^*$ transition involving a combination such as $xy(\pi^*) \rightarrow L(\pi^*)$ and yz, $xz(\pi^*)$ $L(\pi^*)$; on the other hand the highest energy bands have been assigned to a L → M CT band generated from a combination $L(\pi^*) \rightarrow x^2\text{-}y^2(\sigma^*)$ and $L(\sigma) \rightarrow x^2\text{-}y^2(\sigma^*)$ transitions.

Complex III shows a band at 276 nm probably due to $\pi \rightarrow \pi^*$ transitions of the phenyl group in the triphenylphosphine ligand.

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